

Supporting information

Green synthesis of porous Au-N_x-TiO₂ nanospheres for solar light induced photocatalytic degradation of diazo, triazo dyes and their eco-toxic effects

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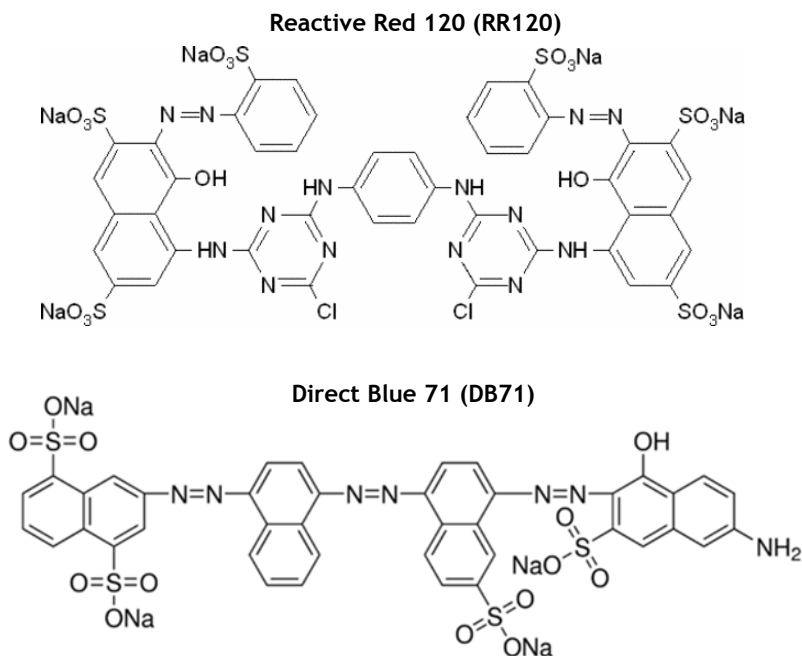


Fig. S1. The molecular structures for the model pollutants (diazo (RR120) and triazo dyes (DB71)).

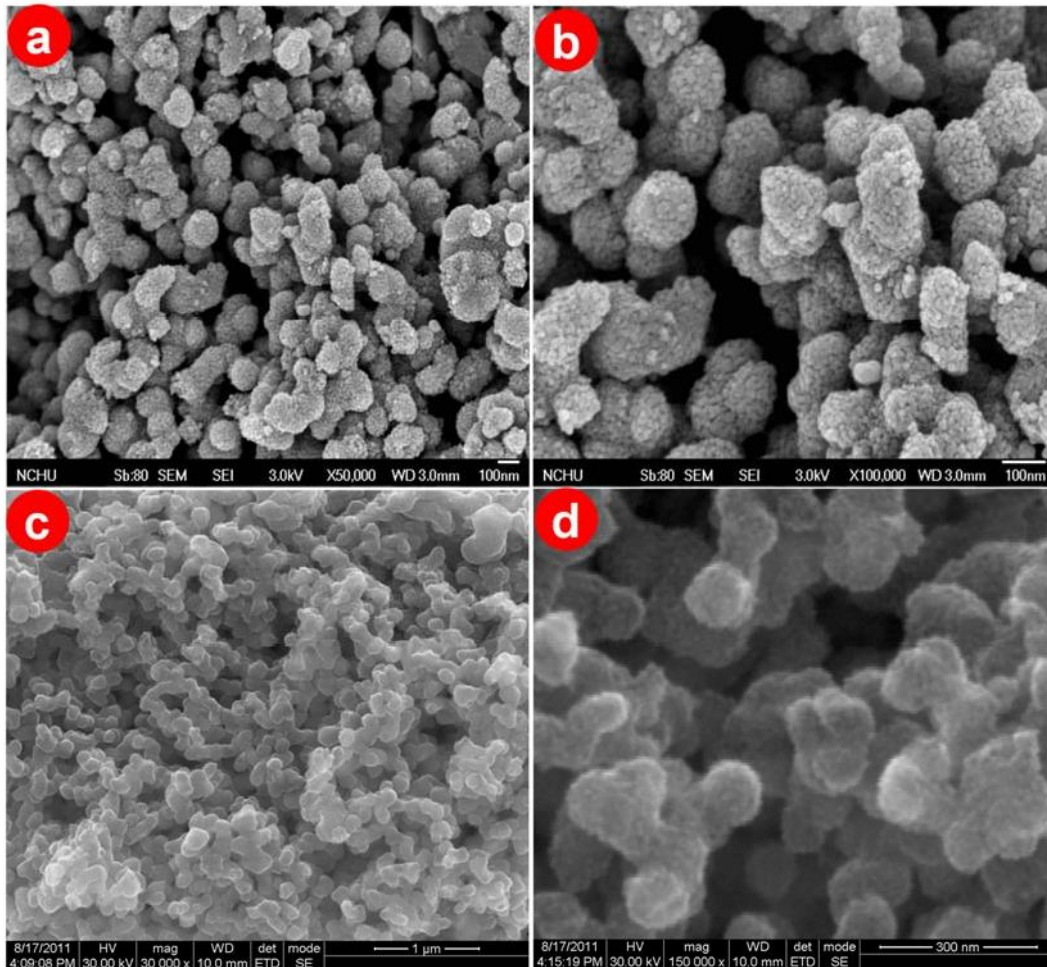


Fig. S2. SEM images of porous TiO₂ NSPs (a,b) and N_x-TiO₂ NSPs (c,d).

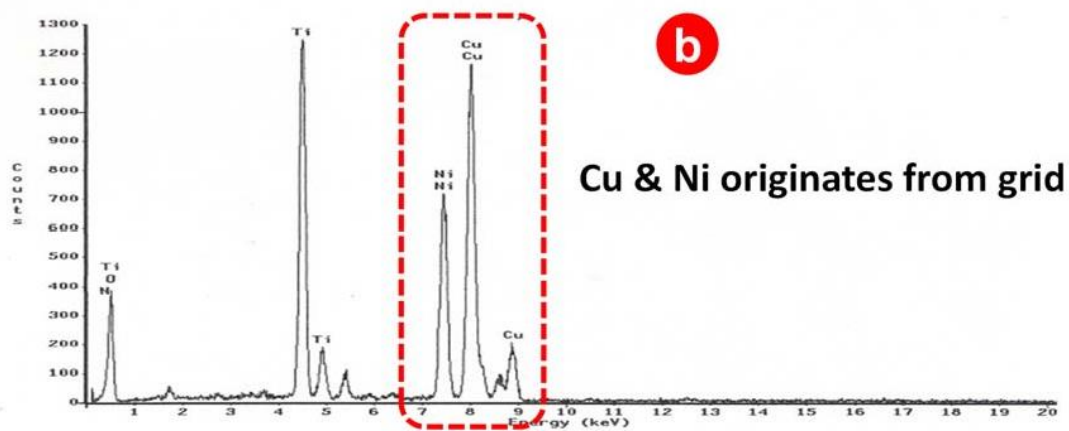
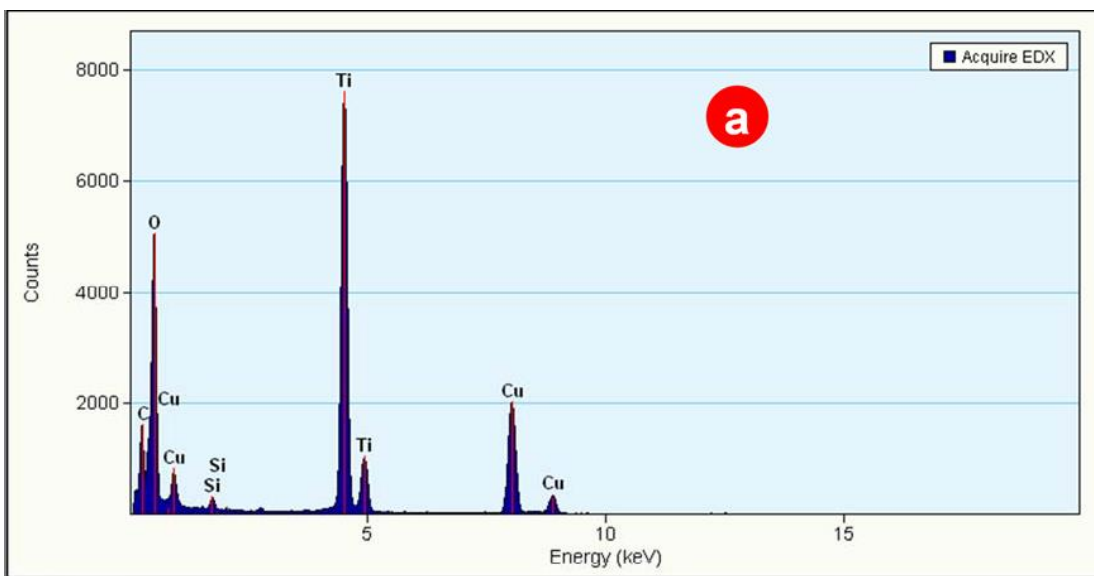


Fig. S3. EDAX spectra of porous TiO₂ NSPs (a) and N_x-TiO₂ NSPs (b).

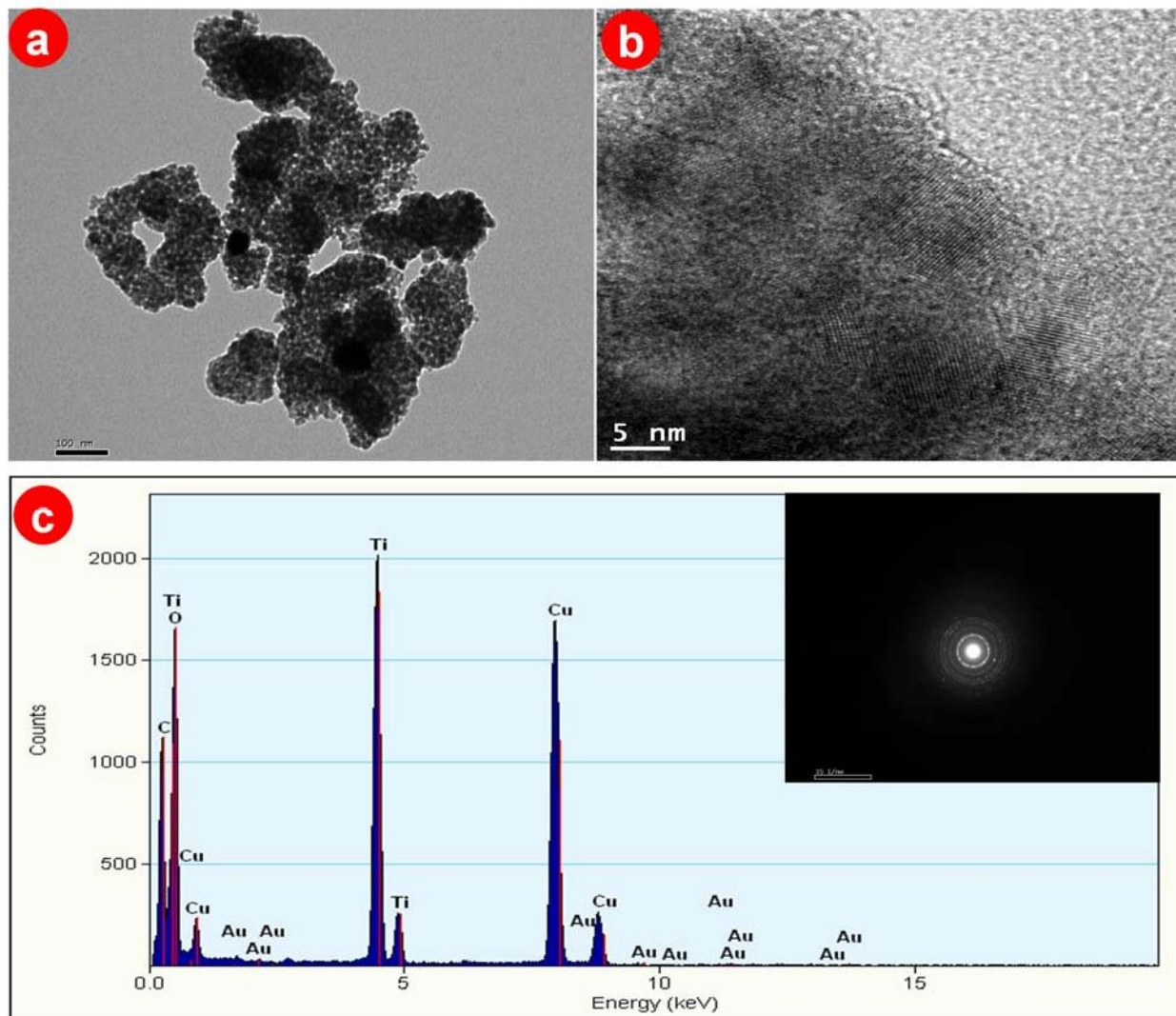


Fig. S4. TEM images (a), HRTEM image (b), EDAX spectrum (c) of porous Au-TiO₂ NSPs.

Inset (c): Corresponding SAED pattern.

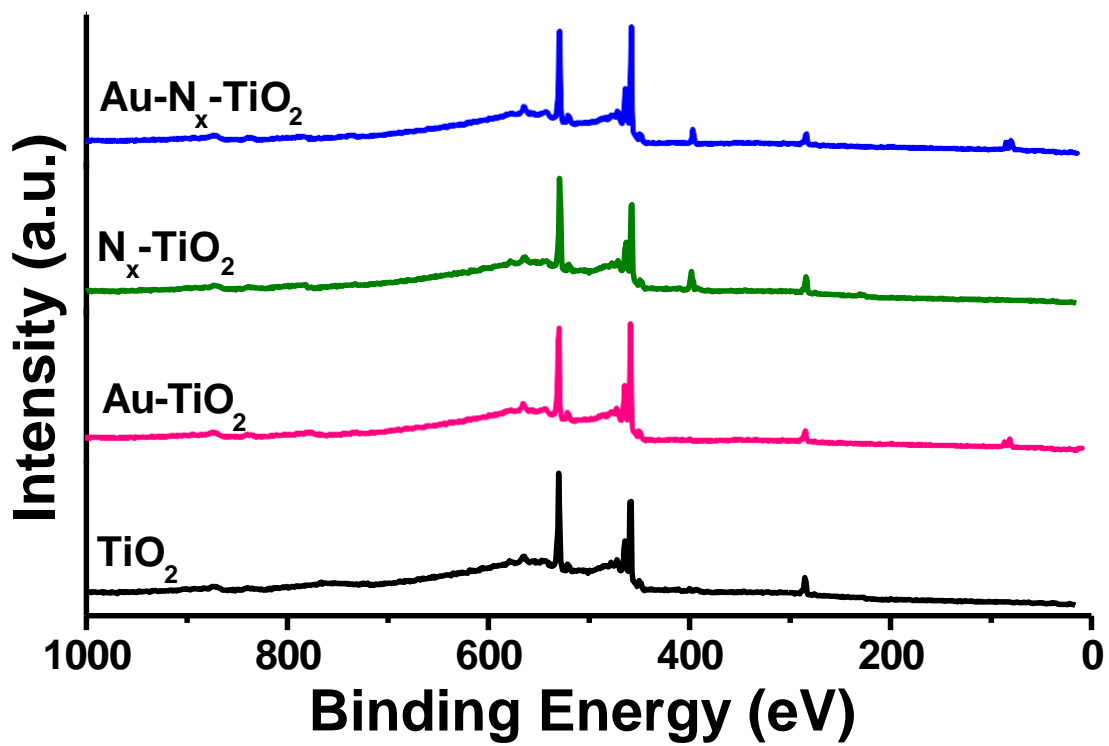


Fig. S5. XPS survey spectra of prepared photocatalysts.

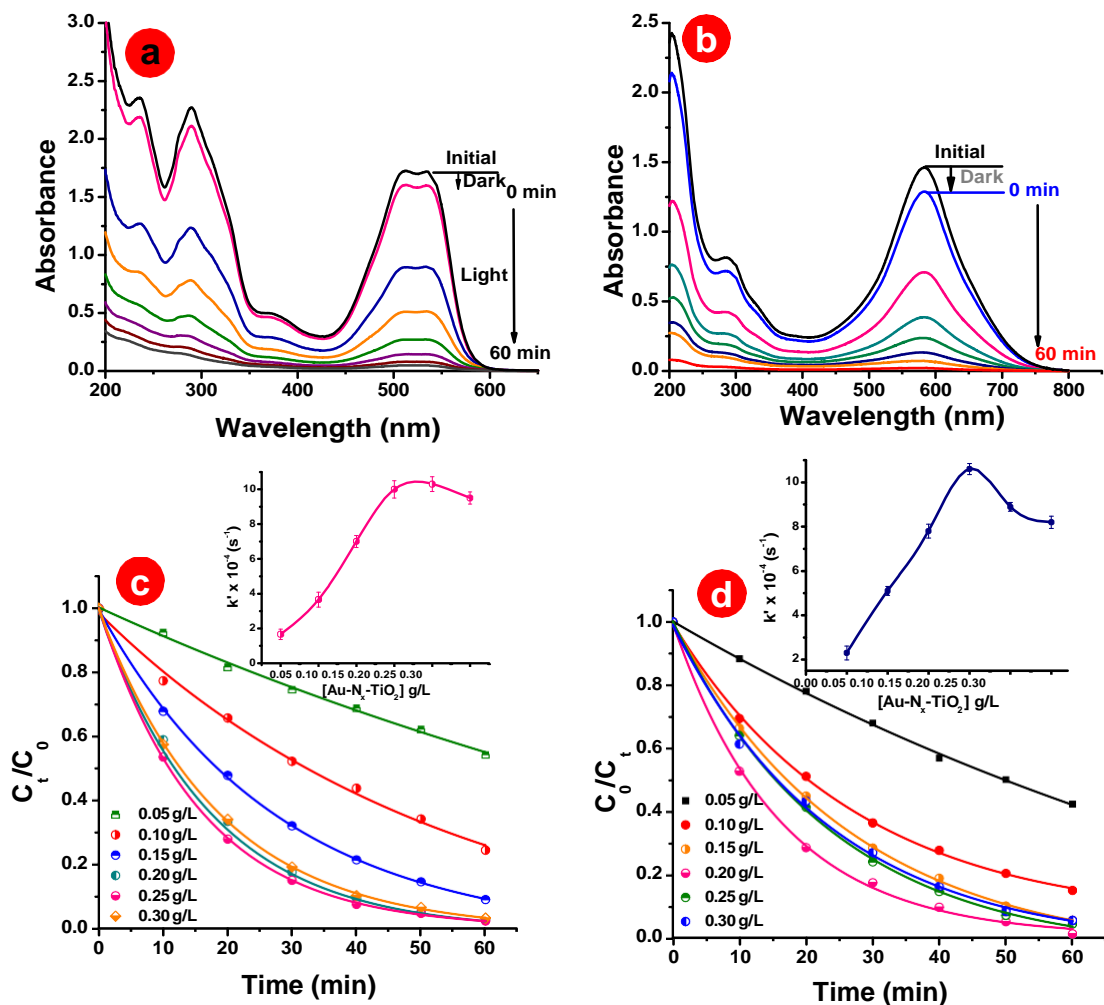


Fig. S6. UV-visible spectra of RR120 (a), DB71 (b) at different irradiation periods in the presence of porous Au-N_x-TiO₂ NSPs. [Dyes] = 4×10^{-5} M and [Au-N_x-TiO₂ NSPs] = 0.2 g L^{-1} . Plot of (C/C₀) vs. time for the photocatalytic degradation of RR120 (c) and DB71 (d) at various concentration of porous Au-N_x-TiO₂ NSPs [Dye] = 4×10^{-5} M. Inset: corresponding rate constant plot. Error bars are the standard deviations of triplicate experiments.

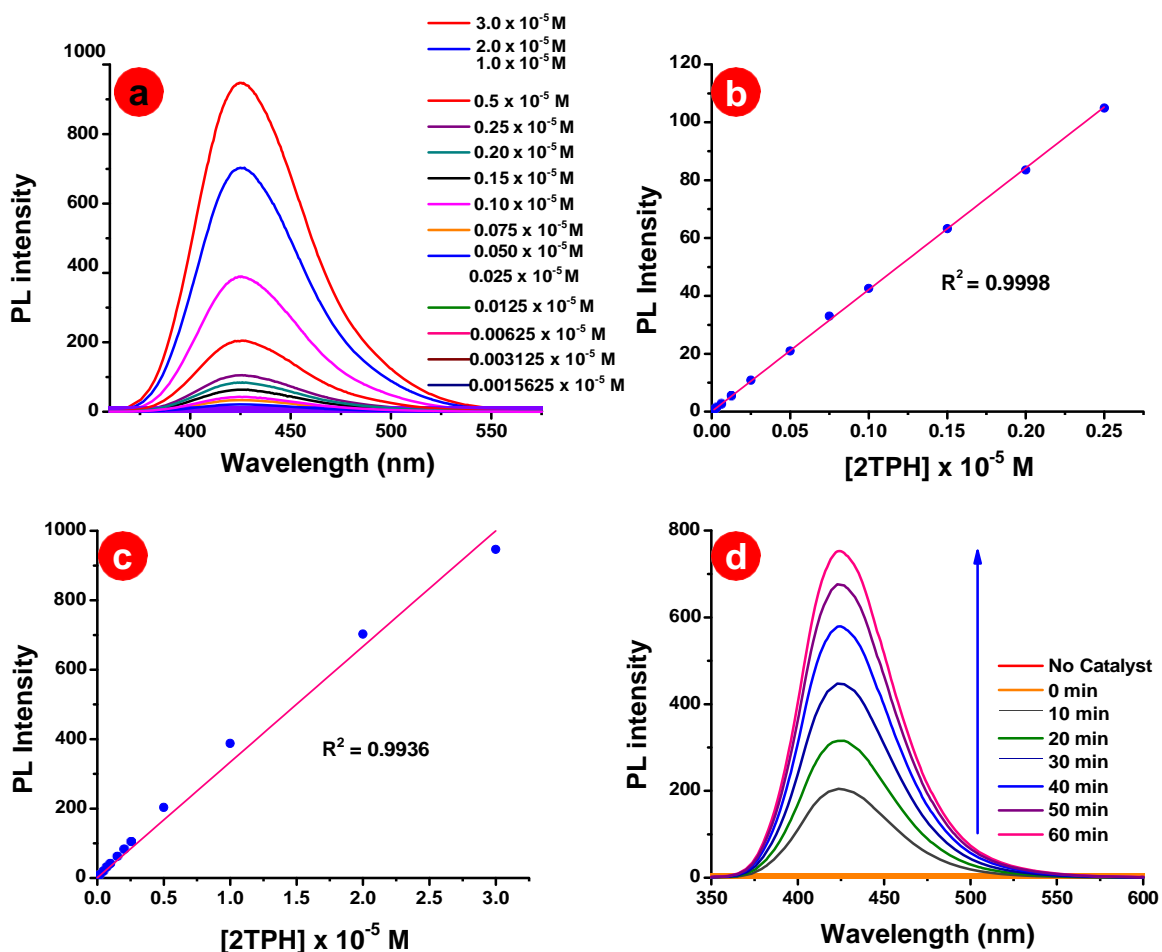


Fig. S7. PL spectra of 2-hydroxy terephthalic acid (standard) at various concentrations (a), fluorescence calibration curves as a function of 2-hydroxy terephthalic acid concentration (b,c), PL spectra of terephthalic acid at various irradiation times in the presence of porous $Au-N_x-TiO_2$ NSPs (d). [Catalysts] = 0.2 g L^{-1} ; [TA] = 5×10^{-4} M.

Table S8. Summary of the results obtained for the amount of photocatalytic degradation of azo dyes and formation of HO• radical in the presence of various catalysts. (*The reaction parameters are identical in the dye degradation and HO• radical quantification*)

Irradiation	Catalyst (0.2 g L ⁻¹)	Amount of HO• radical formation (10 ⁻⁵ M)	Amount of degradation (10 ⁻⁵ M)	
			RR120	DB71
Direct Solar light	TiO ₂ (Degussa P25)	0.33 ± 0.04	1.80 ± 0.05	2.40 ± 0.02
	Porous TiO ₂ NSPs	0.47 ± 0.03	1.95 ± 0.05	2.50 ± 0.01
	Porous N _x -TiO ₂ NSPs	0.89 ± 0.05	2.79 ± 0.13	2.76 ± 0.08
	Porous Au-TiO ₂ NSPs	1.21 ± 0.03	3.36 ± 0.09	3.44 ± 0.04
	Porous Au-N_x-TiO₂ NSPs	1.79 ± 0.05	3.90 ± 0.08	3.94 ± 0.02
Solar (visible) light (λ > 395 nm)	TiO ₂ (Degussa P25)	0.05 ± 0.01	0.40 ± 0.03	0.46 ± 0.01
	Porous TiO ₂ NSPs	0.07 ± 0.01	0.44 ± 0.02	0.48 ± 0.02
	Porous N _x -TiO ₂ NSPs	0.44 ± 0.02	1.04 ± 0.06	1.38 ± 0.04
	Porous Au-TiO ₂ NSPs	0.66 ± 0.02	1.30 ± 0.03	1.70 ± 0.06
	Porous Au-N_x-TiO₂ NSPs	1.32 ± 0.01	3.32 ± 0.05	3.52 ± 0.02

S9: The principle involved in the photocatalytic degradation is the formation of HO• radicals by the utilization of the photocatalytically generated excitons. In this context, the photocatalytically generated HO• radicals in the presence of Au-N_x-TiO₂ NSPs on the direct solar light irradiation is identified and quantified through the photoluminescence (PL) technique. Terephthalic acid (TA) was used as the probe molecule and a change in the PL intensity of the photocatalytically formed 2-hydroxyterephthalic acid is directly proportional to the amount of the HO• produced during the photocatalytic reaction. The qualitative identification of the HO• radicals during the photocatalytic degradation reaction has been reported elsewhere¹⁻⁴. It is important to quantify the photocatalytically generated HO• radicals. The experiments are carried out carefully to make a calibration curve using 2-hydroxyterephthalic acid as shown in **Fig. S7a-c**. The linear regression ($R^2 = 0.9998$) of the calibration curve clearly indicated that the PL intensity of the 2-hydroxy terephthalic acid is increased with respect to its concentration upto 0.25×10^{-5} M (**Fig. S7b**) but the linear regression ($R^2 = 0.9936$) slightly deviates at high concentration of 2-hydroxy terephthalic acid (**Fig. S7c**) which may be caused by 2-hydroxy terephthalic acid absorption and/or fluorescence quenching⁵. **Fig. S7d** reveals that there is no remarkable change in the PL intensity ($\lambda_{\text{max}} = 425$ nm) of aqueous TA in the presence of the catalyst under dark as well as light irradiation in the absence of the porous Au-N_x-TiO₂ NSPs. Whereas, the PL intensity of TA is increased in the presence of both solar light irradiation and porous Au-N_x-TiO₂ NSPs in the photocatalytic system due to the formation of 2-hydroxy terephthalic acid through the reaction between TA and the photocatalytically generated hydroxyl radicals (HO•).

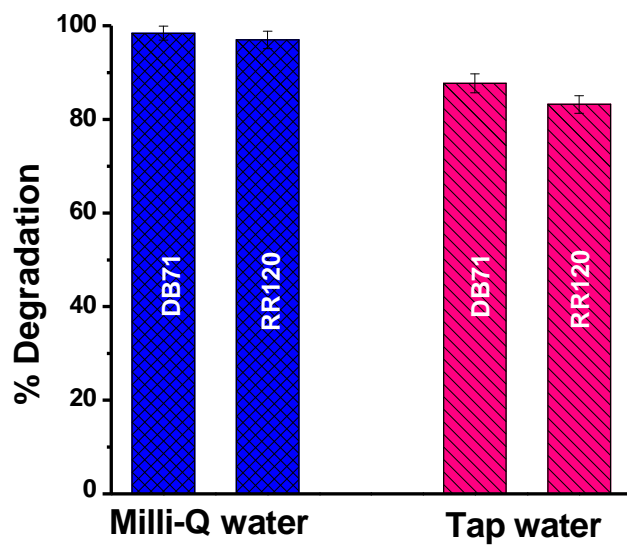


Fig. S10. Histograms showing the percentage degradation of dyes in the presence of Au-N_x-TiO₂ NSPs under direct solar light irradiation. The experiments carried out in the both Milli-Q and tap water and concentrations are maintained as follows: [Catalyst] = 0.2 g L⁻¹; [dye] = 4 × 10⁻⁵ M.

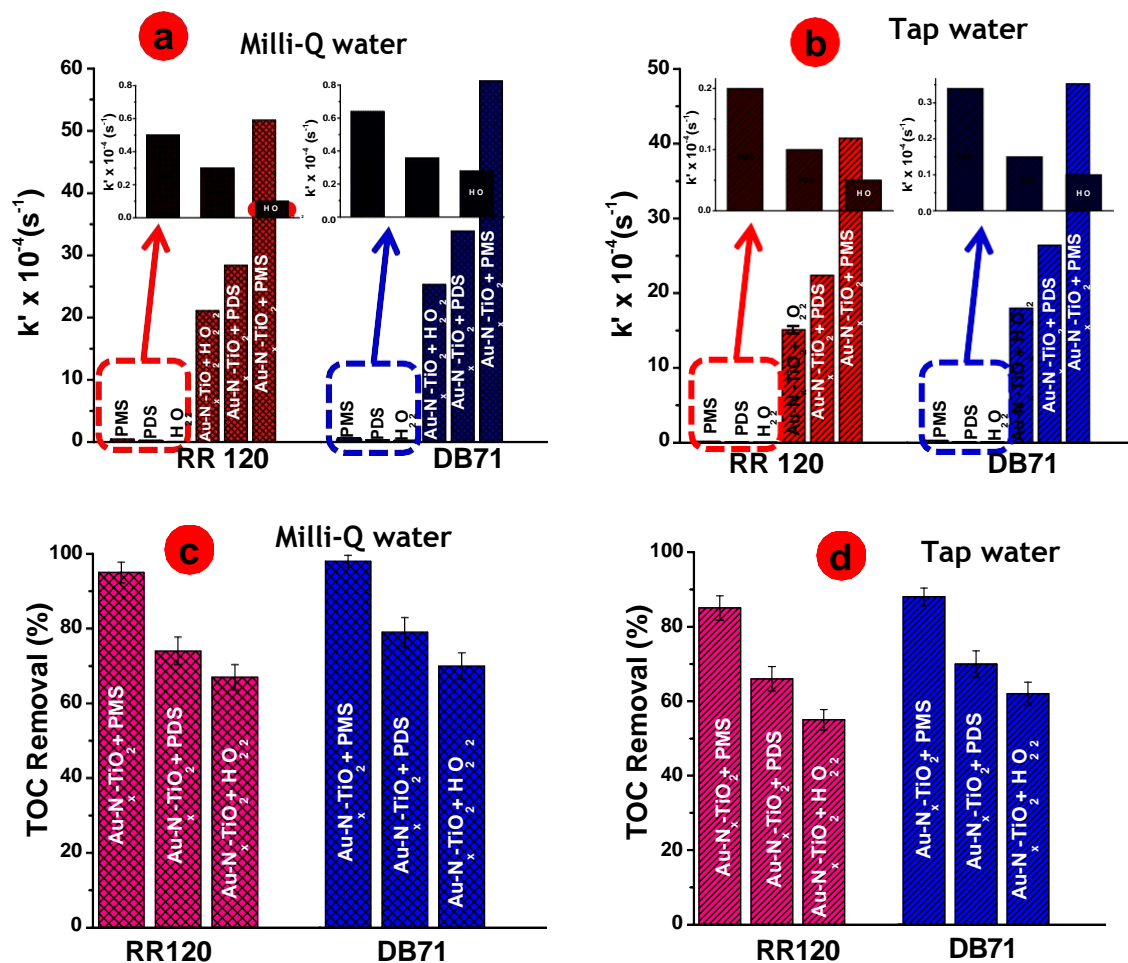


Fig. S11. Histograms showing the comparison of the photocatalytic degradation rate constant (a, b) and mineralization (c,d) of RR120 and DB71 in the presence of oxidants with and without porous Au-N_x-TiO₂ NSPs under direct solar light irradiation. Inset (a,b): maximized area of corresponding plots. The experiments carried out in the both Milli-Q and tap water and concentrations are maintained as follows: [Catalyst] = 0.2 g L⁻¹; [dye] = 4 × 10⁻⁵ M and [Oxidants] = 2.5 × 10⁻⁴ M.

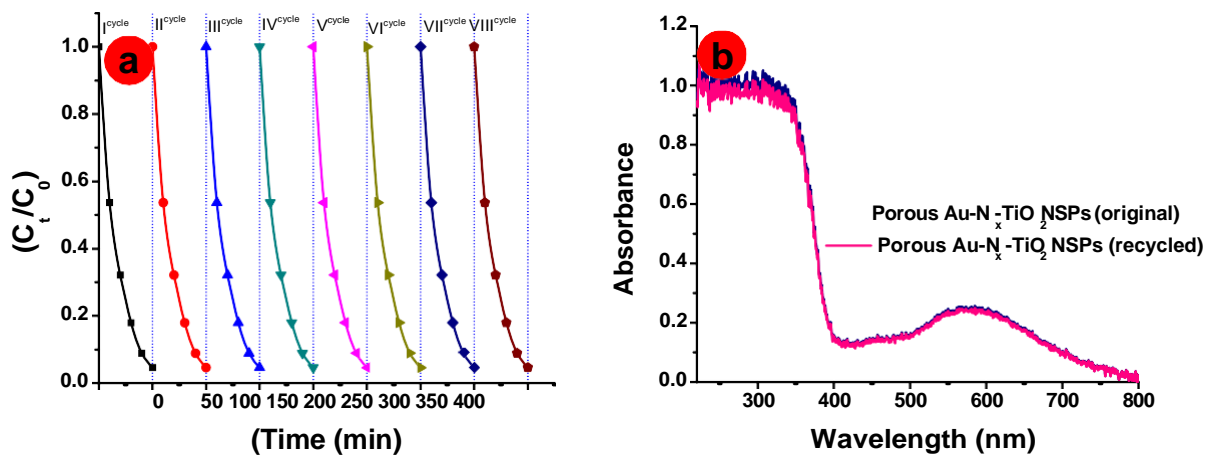


Fig. S12. Photocatalytic degradation of DB71 using recycled porous $\text{Au-N}_x\text{-TiO}_2$ NSPs (a). Initial concentrations: $[\text{Catalyst}] = 0.2 \text{ g L}^{-1}$; $[\text{dye}] = 4 \times 10^{-5} \text{ M}$. DRS of porous $\text{Au-N}_x\text{-TiO}_2$ NSPs before and recycled (b).

References

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